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## COMPLETE SPECIFICATION

### Copolymers

We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America, of 343, State Street, Rochester, New York 14650, United States of America, (Assignee of HUGH JOHN HAGEMeyer, Jr. and MAX STATMAN), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel copolymeric materials containing 2,2,4-trimethyl-3-hydroxypentyl methacrylate. Such copolymers are quite unique in their properties and are especially useful in the formation by relatively simple techniques, of surface coatings and lacquers exhibiting significantly improved properties.

Most monomeric agents when polymerized no longer contain a reactive group and therefore cannot be further reacted. In surface coatings such as lacquers, the polymer must be soluble in the lacquer solvent system. This limits the solvent resistance of the final coating as well as adhesion, hardness etc. In a polymer containing a reactive group, the physical properties of a lacquer may be changed by chemical reactions. This type of lacquer is sometimes called thermosetting. When a suitable "crosslinking" agent is used, improved properties can be obtained. More specifically, these crosslinking agents include; the diisocyanates such as toluene diisocyanate, methylol-urea type resins; methylol-melamine type resins commercially available, e.g. under

the trade name Cymel, methylol-guanamine type resins, resorcinol-formaldehyde resins; hydrazine; diamines; triamines; epoxy resins; polyfunctional acids such as terephthalic and adipic acids, trimellitic anhydride and succinic acid; and diketenes such as the bisdiazido keto-alkanes. It is noted that the present hydroxy polymers can be crosslinked at least to a degree by any polyfunctional material which can react, e.g., by addition or condensation, with the —OH groups of the polymer. Moreover, the application of heat alone would be expected to promote some crosslinking. Lacquers with greater hardness, improved solvent resistance, better adhesion, and improved softening points result from the use of such thermosetting systems.

The polymers of the present invention exhibit significantly improved properties such as solvent resistance, adhesion, and hardness, rendering them highly useful for surface-coating materials;

According to the present invention there is provided a copolymer of 2,2,4-trimethyl-3-hydroxypentyl methacrylate with at least one other unsaturated monomer copolymerizable therewith. The hydroxyl group of the 2,2,4-trimethyl-3-hydroxy pentyl methacrylate does not react during polymerization and standard polymerization techniques may be employed without the formation of gels.

The incorporation of functional groups into copolymers is not new to the art. *Vinyl and Related Polymers* pp. 68—72 and 208—211, discusses the various reasons for such copolymers. None of the functional monomers dis-

- cusssed therein, however, contains a reactive hydroxyl group. The use of  $\beta$ -hydroxyethyl methacrylate and  $\beta$ -hydroxyethyl acrylate in styrene and/or acrylic polymers is discussed in the article by Petropoulos, Frazier, and Cadwell in the Federation of Societies for Paint Technology's *Official Digest* June, 1961, pp. 719—731, but none of these copolymers has led to a commercially successful product.
- 10 Copolymers from one or more unsaturated monomers and 2,2,4-trimethyl-3-hydroxypentyl methacrylate may be easily made, using techniques commonly known. Solution polymerization techniques allow the formation of
- 15 polymers containing any practical amount of 2,2,4-trimethyl-3-hydroxypentyl methacrylate. The comonomers useful in the present invention are those containing  $\text{CH}_2=\text{C}$ ,  $\text{>C}=\text{C}<$ , or  $\text{>C}=\text{C}-\text{C}=\text{C}<$  types of unsaturation. A fairly comprehensive list of such monomers is set forth in U.S. Patent Specification No. 2,396,785. It is noted that some of these monomers are particularly useful when used alone with the 2,2,4-trimethyl-3-hydroxypentyl methacrylate, while others give useful products when employed in ternary or higher monomer systems or as modifiers in relatively small amounts. The proportions thereof employed will of course depend upon the particular use of the polymer contemplated. It is generally preferred, however, that from 5 to 50% by weight of the copolymer be comprised of the hydroxypentyl methacrylate. It is noted that the polymer examples given
- 35 herein are intended to illustrate some of the useful effects of the said hydroxypentyl methacrylate on polymers and not as limiting the copolymerizability thereof to less than an almost infinite variety of addition polymerizable materials. The following Tables I, II, and III specifically name some of the useful comonomers.

TABLE I  
Some Representative Acrylates and Methacrylates Suitable for Copolymerization.

- 45 *Halogen-containing Aliphatics*  
 $\beta$ -Bromoethyl  
Monofluoroethyl  
50 2,2,2-Trifluoroisopropyl  
2,2,2-Trifluoroethyl  
2,2-Dichloroethyl
- Phenyl-substituted Aliphatics*  
 $\beta$ -Phenylethyl  
55  $\alpha$ -Phenylethyl
- Alicyclic*  
Cyclohexyl  
o-Chlorocyclohexyl  
2-Methylcyclohexyl  
60 Cyclobutyl  
Cyclopentyl  
Furfuryl

*Phenyl or Aromatic*

- Phenyl  
65 Pentachlorophenyl  
 $\alpha$ -Naphthyl  
 $\beta$ -Naphthyl  
Benzyl  
 $\alpha$ -Methylbenzyl  
o-Cresyl  
70 m-Cresyl  
p-Bromophenyl  
Ethylbenzyl  
Isopropylbenzyl

TABLE II

Styrene, Halogenated Styrenes, Alkyl Derivatives of Styrene, Halogenated Derivatives of Alkyl Derivatives of Styrene and other Related Monomers Suitable for Reaction

- Styrene  
 $\alpha$ -Methylstyrene  
2-Chloro- $\alpha$ -methylstyrene  
4-Chloro- $\alpha$ -methylstyrene  
85 2,3-Dimethyl- $\alpha$ -methylstyrene  
2,4-Dimethyl- $\alpha$ -methylstyrene  
4-Isopropyl- $\alpha$ -methylstyrene  
3-Chloro-2-methylstyrene  
2,5-Dichloromethylstyrene  
90  $\beta$ -Methylstyrene  
3-Ethylstyrene  
p-Chlorostyrene  
2,5-Dichlorostyrene  
Trichlorostyrenes  
95 Vinylnaphthalenes, e.g.  $\beta$ -vinylnaphthalene  
Halogenated Vinylnaphthalenes

TABLE III

Additional Comonomers

- Acrylonitrile  
Methacrylonitrile  
Vinyl Esters  
Vinyl Acetate  
Vinyl Propionate  
105 Vinyl Butyrate  
Vinyl Isobutyrate  
Vinyl 2-Ethylhexanoate  
Vinyl Ethers  
Vinyl Methyl Ether  
Vinyl Ethyl Ether  
110 Vinyl Isopropyl Ether  
Vinyl Isobutyl Ether  
Vinyl 2-Ethylhexyl Ether  
Ethylene  
Propylene  
115 Isobutylene and other olefins  
Butadiene  
Tetramethylbutadiene and other dienes  
Chloroprene and other halogenated dienes  
Isoprene  
120 Diethyl Maleate and other alkyl esters of maleic acid  
Diethyl Fumarate and other alkyl esters of fumaric acid

Vinyl Chloride  
Vinylidene Chloride  
Vinyl Fluoride  
Vinyl Bromide

- 5 It is noted that many of the above materials do not necessarily provide lacquers. However, they find utility in other fields such as moulding plastics and fibres.

- 10 The preparation of the monomethacrylate ester of 2,2,4-trimethyl-1,3-pentanediol is carried out using either conventional ester interchange or direct esterification reaction conditions. In the ester interchange process, 2,2,4-trimethyl-1,3-pentanediol is reacted with
- 15 methyl methacrylate using either acidic or basic catalysts at concentrations of from 0.5 to 5 percent. The reaction temperature can be controlled by the combination or separate use of reduced pressures, an inert diluent or an excess
- 20 of methyl methacrylate. Methanol is removed as formed. After catalyst removal, the pure methacrylate esters (both the mono and diesters are formed) of 2,2,4-trimethyl-1,3-pentanediol are isolated by distillation at reduced
- 25 pressure. Alternatively, 2,2,4-trimethyl-1,3-pentanediol may be esterified with methacrylic acid using an acidic catalyst. In either process, a stabilizer such as hydroquinone may be used to inhibit polymerization. Particular co-
- 30 polymers provided by the present invention have the following component ranges:—(a) 5—50% by weight 2,2,4-trimethyl-3-hydroxypentyl methacrylate and 95—50% by weight methyl methacrylate, (b) 20—80% by weight
- 35 styrene, 10—50% by weight 2,2,4-trimethyl-3-hydroxypentyl methacrylate and 0—50% by weight acrylic ester, (c) as (b) but in which the acrylic ester is replaced by a methacrylic ester.

- 40 The following Example illustrates the preparation of 2,2,4-trimethyl-3-hydroxypentyl methacrylate.

#### EXAMPLE 1

- A mixture consisting of 146 grams (1 mole) of 2,2,4-trimethyl-1,3-pentanediol, 500 grams
- 45 (5 moles) of methyl methacrylate, and 3 grams (0.6 percent, based on methyl methacrylate) of hydroquinone was charged to a one-litre flask fitted with a pressure-equalizing dropping funnel, a thermometer, and a capillary tube for
- 50 the introduction of air. The funnel was charged with a 2.0 N solution of sodium methoxide in methanol and the apparatus attached to a 10-tray Oldershaw column fitted with a variable-reflux head. The mixture was heated to
- 55 60° C. under a pressure of 200 mm., and 10 ml. of this sodium methoxide solution was introduced. When the vapours at the head of the column reached 34° C. (the boiling point of the methanol-methyl methacrylate azeotrope at 200 mm.), the head was adjusted for 50
- 60 per cent take-off. Catalyst solution was added in small amounts to the reaction mixture during the entire six-hour reaction period until 30

ml. had been added. The base temperature ranged from 55—70° C., and the head temperature remained constant at 34° C. The reaction mixture was then neutralized with dilute acetic acid and washed with water and saturated salt solution. The excess methyl methacrylate was flashed at reduced pressure, and after adding hydroquinone (3 percent) the residue was distilled to give 133 grams of the monomethacrylate of 2,2,4-trimethyl-1,3-pentanediol and 113 grams of the dimethacrylate ester.

The following Examples will further illustrate but in no manner limit, the invention. Examples 2, 3, 5 and 7—10 are comparative.

#### EXAMPLE 2

The Polymerization of Methyl Methacrylate  
Into a suitable reaction system consisting of a stirred flask equipped with a thermostatically controlled heater and an inert gas system to exclude oxygen, the following materials were reacted for 24 hours at 60° C.; methyl methacrylate, 280 ml.; toluene, 700 ml.; and benzoyl peroxide, 2 grams. The resultant polymer solution was a clear, viscous liquid containing 30 percent solids. The solid polymer had an I.V. of 0.33. A sample of this liquid was cast into a film of 10-mil thickness when wet and allowed to air dry. This produced a brittle film with little resistance to solvents such as acetone, alcohols, etc. A sample of this polymeric solution was mixed with toluene diisocyanate, 10 percent by weight based on methyl methacrylate. This material was cast into a film and allowed to air dry. Upon drying, the film was cured in an oven for 30 minutes at 300° F. No change in physical properties was noted.

#### EXAMPLE 3

A Thermosetting Lacquer Made Using the Polymer Produced in Example 2

A sample of polymer solution from Example 2 was mixed with a "crosslinking" agent. Cyanamid's Cymel 300 (melamine-formaldehyde resin) to give 20 weight percent Cymel based on total solids and one percent of para-toluene sulphonic acid was added. The mixture was cast onto a glass plate to give a film which was 3 mils thick upon drying. This film was then cured at 300° F. for 30 minutes. This film was soft and had poor solvent resistance, especially with acetone.

#### EXAMPLE 4

Copolymer Containing 80 Percent Methyl Methacrylate and 20 Percent 2,2,4-Trimethyl-3-hydroxypentyl Methacrylate

Using the system described in Example 1, methyl methacrylate, 200 ml.; toluene, 625 ml.; 2,2,4-trimethyl-3-hydroxypentyl methacrylate, 50 ml.; and benzoyl peroxide, 2 grams; were reacted for 24 hours at 60° C. The resultant polymer solution was a clear, viscous

liquid containing 32 percent solids. The polymer had an I.V. of 0.32.

#### EXAMPLE 5

##### 5 A Thermosetting Lacquer Made Using the Polymer Produced in Example 3

A thermosetting lacquer was made and tested in the manner described in Example 2 excepting that the copolymer from Example 3 was used. This produced a film which showed better hardness than Example 2. Also, it showed scuff resistance and excellent acetone resistance. See TABLE I for comparative data.

#### EXAMPLE 6

##### 15 A Copolymer Containing Methyl Acrylate, Methyl Methacrylate, and 2,2,4-Trimethyl-3-hydroxypentyl Methacrylate Using the Suspension Polymerization Technique.

Into a suitable reaction system the following mixture was reacted: Water, 245 ml.; sodium hydroxide, 1.5 grams; phosphoric acid (85 percent), 1.3 ml.; gum arabic, 2 grams; methyl acrylate, 60 ml.; methyl methacrylate, 120 ml.; 2,2,4-trimethyl-3-hydroxypentyl methacrylate, 40 ml.; and benzoyl peroxide, 1.6 grams; at 85° C. for 3 hours. The product was a polymer in fine particulate form. A sample of this polymer was dissolved in toluene to give a solution containing 30 percent solids. The solution was tested in a manner described in Examples 2 and 4. The results showed excellent hardness scuff resistance, and acetone resistance. Comparative data is given in TABLE I.

#### EXAMPLE 7

##### 35 A Copolymer Containing Methyl Acrylate, Methyl Methacrylate and 2-Hydroxyethyl Methacrylate

Using the system described in Example 6, a copolymer was prepared using the same recipe as Example 6 excepting 40 ml. of 2-hydroxyethyl methacrylate was substituted for the 2,2,4-trimethyl 3-hydroxypentyl methacrylate. The resultant white polymer was in fine particulate form and would not dissolve in toluene even to the extent of 3 percent. Testing as a lacquer was impossible.

#### EXAMPLE 8

##### 50 A Copolymer Containing 80 Percent Methyl Methacrylate and 20 Percent 2-Hydroxyethyl Methacrylate

Using the system described in Example 2, the recipe of Example 3 was repeated excepting 50 ml. of 2-hydroxyethyl methacrylate was

substituted for the 2,2,4-trimethyl-3-hydroxypentyl methacrylate. The resultant product was not a clear viscous solution. A thick, almost solid gel had formed which could not be poured from the flask. This material was not suitable for testing as a lacquer.

#### EXAMPLE 9

##### 60 A Copolymer Containing 80 Percent Methyl Methacrylate and 20 Percent 2-Hydroxypropyl methacrylate

Using the procedure and recipe of Example 8, 2-hydroxypropyl methacrylate was substituted for the 2-hydroxyethyl methacrylate. Once again the resultant polymer solution was a thick gel and not suitable for testing.

#### EXAMPLE 10

##### 70 A Copolymer Containing 80 Percent Methyl Methacrylate and 20 Percent 2,2-Dimethyl-3-hydroxypropyl Methacrylate

Using the procedure and recipe of Example 8, 2,2-dimethyl-3-hydroxypropyl methacrylate was substituted for the 2-hydroxyethyl methacrylate. Again the resultant polymer solution was a thick gel and not suitable for testing.

Examples 4 to 10 demonstrate the uniqueness of the present invention. While the polymers described in Examples 7 to 10 were made using hydroxyl containing monomers, a suitable lacquer base did not result. In two different types of polymerization techniques, solution and suspension, the 2,2,4-trimethyl-3-hydroxypentyl methacrylate was able to form lacquer usable in industry. The ease in which our invention can be incorporated in currently used polymer systems is a most important aspect.

#### EXAMPLE 11

##### 90 A Copolymer Containing 67 Percent Styrene, 19 Percent n-Butyl Methacrylate and 14 Percent 2,2,4-Trimethyl-3-Hydroxypentyl Methacrylate

Into a suitable reaction system was reacted 600 ml. of isobutyl alcohol, 76 ml. of n-butyl methacrylate, 225 ml. of styrene, 53 ml. of 2,2,4-trimethyl-3-hydroxypentyl methacrylate, 3 ml. of dodecyl mercaptan, and 8 ml. of cumene hydroperoxide at 112° C. for 6 hours. Xylene, 250 ml., was then added to the resultant mixture to produce a lacquer solution containing 34 percent solids. This copolymer was tested in a manner described in Example 3. The resultant film was quite hard and showed excellent solvent resistance. See TABLE IV.

TABLE IV  
Properties of Thermosetting Lacquer

Example No.	Hardness	Scuff	Acetone Resistance
3	H	Poor	Poor
5	4H	Excellent	Excellent
6	5H	Excellent	Excellent
11	4H	Excellent	Excellent

5 In the above table, hardness is a measure of surface hardness and is expressed as the hardest grade of pencil which will not scratch the film surface; scuff is a measure of softening point as well as hardness. This test is made by vigorously scratching the film's surface with one's fingernail and examining the scratch mark; and the resistance of a film to acetone attack is a measure of compatability, crosslinking, and internal stress.

#### EXAMPLE 12

10 A Copolymer Containing 60 Percent Methyl Methacrylate and 40 Percent 2,2,4-Trimethyl-3-Hydroxypentyl Methacrylate  
15 Using the procedure described in Example 4, a copolymer was produced containing 40

percent 2,2,4-trimethyl-3-hydroxypentyl methacrylate. The copolymer (and also those in Examples 13 to 43) were thermoset using Cymel 200 as cross-linking agent. Upon testing as in Example 3, this copolymer gave an excellent film comparable to those produced from Examples 5 and 6.

20 The following additional Examples were made following the procedure and recipe of Example 4 excepting other monomers were substituted for the methyl methacrylate constituent. In each example 625 ml. toluene, 50 ml. 2,2,4-trimethyl-3-hydroxypentyl methacrylate, and 2 grams of benzoyl peroxide were reacted at 60° C. for 24 hours with the given comonomer.

Exam. No.	Monomer	Tested Thermosetting Lacquer		
		Hardness	Scuff	Acetone Resistance
13	Methyl Acrylate	3H	Excellent	Excellent
14	Ethyl Acrylate	3H	Excellent	Excellent
15	n-Butyl Methacrylate	4H	Excellent	Excellent
16	2-Ethylhexyl Methacrylate	4H	Excellent	Excellent
17	Hexyl Methacrylate	4H	Excellent	Excellent
18	Hexyl Acrylate	3H	Excellent	Excellent
19	Cyclohexyl Methacrylate	4H	Excellent	Excellent

#### EXAMPLE 20

35 A Polymer Containing Methyl Methacrylate, Methyl Acrylate and 2,2,4-Trimethyl-3-Hydroxypentyl Methacrylate  
40 Into a suitable reaction system such as described in Example 2 was reacted 700 ml. of toluene, 120 ml. of methyl methacrylate,

120 ml. of methyl acrylate, 40 ml. of 2,2,4-trimethyl-3-hydroxypentyl methacrylate, and 2 grams of benzoyl peroxide for 24 hours at 60° C. The resultant polymeric solution contained 30 percent solids. The solids contained 13.6 percent hydroxy pentyl methacrylate and 44.2 percent methyl acrylate and showed an I.V. of

0.36. The resultant polymer gave an excellent film when tested as a thermosetting lacquer. In the following Examples the styrene-2,2,4-

trimethyl-3-hydroxypentyl methacrylate monomer system is polymerized with or without additional monomers. 5

	Example Number				
	21	22	23	24	25
Isobutyl Alcohol, ml.	600	600	600	600	600
Styrene, ml.	225	260	225	225	225
2,2,4-Trimethyl-3-hydroxypentyl Methacrylate, ml.	53	70	53	53	53
Methyl Acrylate, ml.	76	—	35	—	—
Methyl Methacrylate, ml.	—	—	40	—	—
2-Ethylhexyl Methacrylate, ml.	—	—	—	76	—
Ethyl Acrylate, ml.	—	—	—	—	76
Dodecyl Mercaptan, ml.	3	3	3	3	3
Cumene Hydroperoxide, ml.	8	8	8	8	8
Temperature, C.	112	116	114	111	112
Length of Run, hrs.	6	6	6	6	6
Xylene Added, ml.	250	250	250	250	250
Properties of Crosslinked Film					
Hardness	3H	5H	5H	4H	3H
Scuff	Excellent	Excellent	Excellent	Excellent	Excellent
Acetone Resistance	Excellent	Good	Excellent	Excellent	Excellent

#### EXAMPLE 26

10 A Copolymer Containing 70 Percent  $\beta$ -Bromoethyl Methacrylate and 30 Percent 2,2,4-Trimethyl-3-hydroxypentyl Methacrylate

15 Into a suitable reaction system consisting of a stirred flask equipped with a thermostatically controlled heater and an inert gas system to exclude oxygen, the following materials were placed and reacted for 24 hours at 60° C.: toluene, 300 ml.;  $\beta$ -bromoethyl methacrylate, 90 grams; 2,2,4-trimethyl-3-hydroxypentyl methacrylate, 35 grams; and benzoyl peroxide, 2 grams. The resultant polymer solution was

a clear, viscous liquid containing 30 percent solids. When this material was tested as a thermosetting lacquer, excellent properties resulted. 25

The following Examples were carried out using the procedure and recipe of Example 26 excepting other monomers were substituted for the 90 grams of  $\beta$ -bromoethyl methacrylate constituent. In each Example, 300 ml. of toluene, 35 grams of 2,2,4-trimethyl-3-hydroxypentyl methacrylate, and 2 grams of benzoyl peroxide were reacted at 60° C. for 24 hours with the given comonomer. 30

Ex.	Monomer	Tested Hardness	Thermosetting Scuff	Lacquer Acetone
27	2,2-Dichloroethyl Methacrylate	4H	Excellent	Excellent
28	$\beta$ -Phenylethyl Acrylate	2H	Good	Excellent
29	Cyclohexyl Acrylate	3H	Excellent	Excellent
30	Furfuryl Methacrylate	4H	Excellent	Excellent
31	2-Methylcyclohexyl Methacrylate	3H	Excellent	Excellent
32	Cyclopentyl Acrylate	3H	Excellent	Excellent
33	Phenyl Methacrylate	3H	Excellent	Excellent
34	Benzyl Acrylate	2H	Good	Excellent
35	o-Chlorobenzyl Methacrylate	3H	Excellent	Excellent
36	Ethyl Benzyl Methacrylate	3H	Good	Excellent
37	$\alpha$ -Naphthyl Methacrylate	2H	Good	Excellent

## EXAMPLE 38

5 A Polymer Containing Methyl Methacrylate, Methyl Acrylate, 2,2,4-Trimethyl-3-hydroxypentyl Methacrylate, and  $\alpha$ -Methylstyrene

10 Into a reaction system such as described in Example 26 were placed and reacted 300 ml. of isobutyl alcohol, 18 ml. of methyl acrylate, 25 ml. of methyl methacrylate, 27 ml. of 2,2,4-trimethyl-3-hydroxypentyl methacrylate, 120 ml. of  $\alpha$ -methylstyrene, 1.5 ml. of dodecyl mercaptan, and 4 ml. of cumene hydroperoxide at reflux temperature for six hours. At the end of the six hours, 125 ml. of xylene was added to give a clear, viscous solution. When this

material was tested as a thermosetting film, excellent properties were found.

In the following Examples, the procedure and recipe of Example 38 were used excepting other monomers were substituted for the 120 ml. of  $\alpha$ -methylstyrene constituent. In each example, 300 ml. of isobutanol, 18 ml. of methyl acrylate, 25 ml. of methyl methacrylate, 27 ml. of 2,2,4-trimethyl-3-hydroxypentyl methacrylate, 1.5 ml. of dodecyl mercaptan, and 4 ml. of cumene hydroperoxide were reacted with the given monomer. After six hours of refluxing, 125 ml. of xylene was added, and the materials were tested.

Example Number	Monomer	Tested Hardness	Thermosetting Scuff	Lacquer Acetone Resistance
39	2-Chloro- $\alpha$ -Methylstyrene	3H	Excellent	Excellent
40	$\beta$ -Methylstyrene	3H	Excellent	Excellent
41	3-Ethylstyrene	3H	Excellent	Excellent
42	Trichlorostyrenes	4H	Excellent	Excellent
43	$\beta$ -Vinylnaphthalene	2H	Good	Excellent

## EXAMPLE 44

35 A Copolymer Containing Vinyl Chloride and 2,2,4-Trimethyl-3-hydroxypentyl Methacrylate

Into a suitable reaction system were added 1600 grams of water, 370 grams of vinyl

chloride, 20 grams of 2,2,4-trimethyl-3-hydroxypentyl methacrylate, 16 grams of Duponol ME, 2.7 grams of sodium persulphate, 3.2 grams of sodium bisulphite, 2 ml. of trimethyl amine (water solution containing 25 percent amine), and 2.4 ml. of dodecyl mer-

captan. The reaction was run for 24 hours at 50° C. Complete utilization of both monomers was noted, and the copolymer was recovered from the emulsion. Solutions of 30 percent of the copolymer in tetrahydrofuran could be poured and cast into clear films, while solutions containing 15 percent polyvinyl chloride, made by a similar reaction, could not even flow from a bottle.

**EXAMPLE 45**  
A Copolymer of Vinylidene Chloride and 2,2,4 - Trimethyl - 3 - hydroxypentyl Methacrylate

The following emulsion was agitated in a sealed bottle at 28° C. for 10 hours:

Water (Acidified to pH 2.5)	43 g.
Ammonium Persulfate	0.13 g.
Duponol ME	4 g.
Vinylidene Chloride	25 g.
2,2,4-Trimethyl-3-hydroxypentyl Methacrylate	5 g.

The resultant latex was diluted with an equal volume of water and then heated to 90° C. Ten grams of 10 percent aluminum sulfate was added to cause coagulation. This material was a very light straw colour and did not darken when heated to 200° C. A sample of ordinary polyvinylidene chloride would darken and turn brown when heated to 185° C. This improved thermal resistance will be quite useful in molding applications.

**EXAMPLE 46**

A Copolymer Containing Acrylonitrile and 2,2,4 - Trimethyl - 3 - hydroxypentyl Methacrylate

Into a 2000-ml. boiling flask equipped with a stirrer were placed 85 ml. of acrylonitrile, 40 ml. of 2,2,4-trimethyl-3-hydroxypentyl methacrylate, 0.2 ml. of dodecyl mercaptan, 1400 ml. of water, 1 gram of ammonium persulfate, and 0.3 gram of sodium bisulphite. This mixture was reacted at 45° C. for six hours using agitation. Upon cooling, 90 grams of copolymer was recovered. The recovered copolymer was soluble in acetone to the extent of 34 percent and in tetrahydrofuran, 55 percent. A sample of this copolymer when dissolved in dimethyl formamide was spun into a three-denier-per-filament fibre. This fibre compared well with that made from ordinary polyacrylonitrile in most properties and showed exceptional improvements in dye take-up.

**EXAMPLE 47**

A Copolymer Containing Vinyl Acetate and 2,2,4 - Trimethyl - 3 - hydroxypentyl Methacrylate

In a suitable reaction system were reacted, 300 ml. of benzene, 100 grams of vinyl acetate, 1.5 grams of 2,2,4-trimethyl-3-hydroxypentyl methacrylate, and 2 grams of acetyl peroxide

at 78° C. for 24 hours. Some 85 grams of copolymer was recovered. This copolymer showed improved resistance to hydrolysis. After heating 24 hours at 160° C., only 3 percent of the acetate groups was lost compared to 8.5 percent for a similar polyvinyl acetate.

**EXAMPLE 48**

A Terpolymer Containing Isobutyl Vinyl Ether, Diethyl Maleate, and 2,2,4-Trimethyl-3-hydroxypentyl Methacrylate

In a suitable reaction system were reacted 200 grams of benzene, 95 grams of isobutyl vinyl ether, 45 grams of diethyl maleate, 20 grams of 2,2,4-trimethyl-3-hydroxypentyl methacrylate, and 2 grams of benzoyl peroxide at 55° C. for 24 hours. The resultant polymer showed promise in waterproofing leather and as a gelatine substitute in photographic film.

**EXAMPLE 49**

A Copolymer Containing Isobutylene and 2,2,4 - Trimethyl - 3 - Hydroxypentyl Methacrylate

In a suitable system were reacted 300 grams of isobutylene, 250 grams of 2,2,4-trimethyl-3-hydroxypentyl methacrylate, 1300 grams of 2 percent hydroxyoctadecane sulphonic acid sodium salt in water, 2 grams of potassium persulphate, and 10 grams of 30 percent hydrogen peroxide at 50° C. The polymer dispersion obtained was coagulated by adding hydrochloric acid, washed and dried. A rubber-like copolymer resulted.

**EXAMPLE 50**

A Terpolymer Containing Butadiene, Acrylonitrile, and 2,2,4-Trimethyl-3-hydroxypentyl Methacrylate

The following mixture was reacted at 60° C. for 72 hours: butadiene, 64 grams; acrylonitrile, 21 grams; 2,2,4-trimethyl-3-hydroxypentyl methacrylate, 15 grams; hydrochloride of diethylamino-ethoxyoleyl anilide (3 percent), 20 grams; sodium salt of isobutylnaphthalene sulphonic acid (10 percent), 120 grams. A rubber-like product resulted which showed improved solvent resistance over a similar butadiene-acrylonitrile polymer.

**WHAT WE CLAIM IS:—**

1. A copolymer of 2,2,4-trimethyl-3-hydroxypentyl methacrylate and at least one other unsaturated material copolymerizable therewith.

2. A copolymer as claimed in claim 1, in which the other unsaturated material is styrene, a halogenated styrene, an alkyl derivative of styrene, a halogenated derivative of an alkyl derivative of styrene, vinyl naphthalene, a halogenated vinyl naphthalene, acrylonitrile, methacrylonitrile, a vinyl ester, a vinyl ether, an olefin, a diene, a halogenated diene, an alkyl ester of maleic acid, an alkyl ester of fumaric acid, vinyl chloride, vinyl fluoride,



- vinyl bromide, vinylidene chloride, or an aliphatic, halogenated aliphatic, phenyl substituted aliphatic, alicyclic, phenyl or aromatic ester of acrylic or methacrylic acid.
- 5 3. A copolymer of 2,2,4-trimethyl-3-hydroxypentyl methacrylate and styrene.
4. A copolymer of 2,2,4-trimethyl-3-hydroxypentyl methacrylate and methyl methacrylate.
- 10 5. A copolymer of from 5 to 50% by weight of 2,2,4 - trimethyl - 3 - hydroxypentyl methacrylate and from 95 to 50% by weight of methyl methacrylate.
- 15 6. A copolymer of 2,2,4-trimethyl-3-hydroxypentyl methacrylate and methyl acrylate.
7. A copolymer of 2,2,4-trimethyl-3-hydroxypentyl methacrylate and n-butyl methacrylate.
- 20 8. A copolymer of 2,2,4-trimethyl-3-hydroxypentyl methacrylate and ethyl acrylate.
9. A copolymer of 2,2,4-trimethyl-3-hydroxypentyl methacrylate and 2-ethylhexyl methacrylate.
- 25 10. A copolymer of 2,2,4-trimethyl-3-hydroxypentyl methacrylate and cyclohexyl methacrylate.
11. A copolymer of 2,2,4-trimethyl-3-hydroxypentyl methacrylate and hexyl methacrylate.
- 30 12. A copolymer of 2,2,4-trimethyl-3-hydroxypentyl methacrylate and hexyl acrylate.
13. A copolymer of from 20 to 80 percent by weight of styrene, of from 10 to 50 percent by weight of 2,2,4-trimethyl-3-hydroxypentyl methacrylate, and of from 0 to 50 percent by weight of an acrylic ester.
14. A copolymer of from 20 to 80% by weight of styrene, of from 10 to 50% by weight of 2,2,4-trimethyl-3-hydroxypentyl methacrylate, and of from 0 to 50% by weight of a methacrylic ester.
15. A copolymer as claimed in claim 1 substantially as hereinbefore described with reference to any of examples 4,6 and 11 to 50.
16. A method for the preparation of an addition copolymer having functionality as claimed in any of claims 1 to 15 which comprises copolymerizing 2,2,4-trimethyl-3-hydroxypentyl methacrylate and at least one other unsaturated material copolymerizable therewith.
17. A method as claimed in claim 16 substantially as hereinbefore described with reference to any of examples 4, 6, and 11 to 50.
18. A copolymer as claimed in any of claims 1 to 15 which is at least partially cross-linked.
19. A copolymer as claimed in claim 18, in which the cross-linking is achieved by use of a diisocyanate, a methylol-urea resin, a methylol-melamine resin, a methylol-guanamine resin, diketene, a diamine, a triamine, or a dibasic acid.
20. An article coated with a copolymer as claimed in claim 18 or 19.
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